

**PROJECT 325B**

**SUMMARY REPORT**

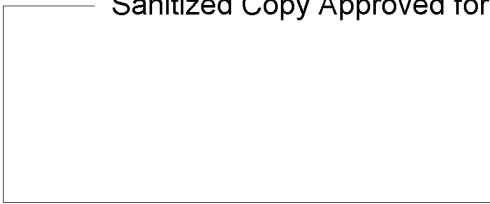
**PERIOD: 1 January 1972 to 31 January 1972**

**Submitted By:**

**Project Manager**

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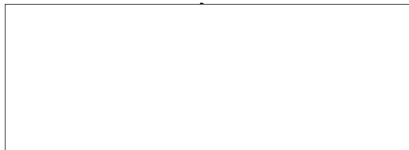


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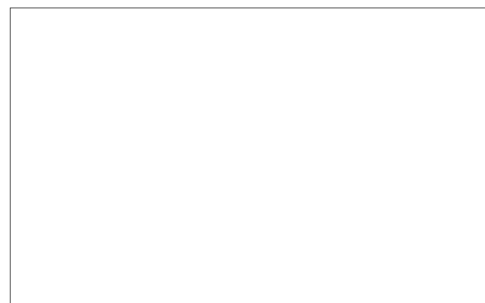
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Project Manager

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## SUMMARY

Project work continued uninterrupted during January. A complete briefing was given at the customer facility covering the entire project from its inception to 1972. A proposal and detailed work statement was submitted for a six month effort with emphasis on the mechanism of shelf life/speed decay. Such work is underway, although no official go ahead has been received. A complete briefing on the work statement was held for the customer at [REDACTED]

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Engineering forecasts completion of the six laboratory HID-2 red light units by 15 February. Detailed experiments have been planned for reactivation studies. Performing these during February and March is dependent on the use of the engineering darkroom; the present environmental contamination level of which prevents such studies. All attempts to reduce the level have not produced significant results. A separate enclosure for such studies is under construction in an isolated area of the building.

The Perkin Elmer interface with sample films was begun. The results to date are encouraging. Detailed results are given in Section 3.0.

## Chemistry

The impurity in D260 which destroys photographic sensitivity is N,N,N',N'-tetramethyl benzidine (TMB).

Its separation from D260 is difficult which explains the difficulties which have been encountered in preparing photo-grade D260 in good yield.

TMB is introduced as an impurity in Michler's hydrol which is an intermediate in the synthesis of D260.

It is not produced during speed decay.

Suitable procedures have been devised for eliminating TMB from Michler's hydrol and also from D260, but the latter is less desirable.

An alternate synthesis of D260 is underway. It circumvents the use of Michler's hydrol and hence the introduction of TMB as an impurity.

Acids have been shown to definitely enhance blotching (high density, irregular fog patterns) to the detriment of image formation.

Bromine in the amount of 8 ppm by weight of  $\text{CBr}_4$  has no effect on sensitometric properties.

Pressure Chemical's polystyrene standard of 200,000 (200K) molecular weight has been found to simulate the photographic properties of MX4500.

Air analysis for the identification of airborne contaminants continues. Incomplete data shows good correlation between poor film and oxidants. Ozone is a probable suspect.

Eleven silicone oils were screened in reference to Dow Corning's DC510 for the elimination of "orange peel" (cf. Ref. 1, 3.3.10, p. 69). One, R631, a product of Union Carbide, is superior to DC510.

## 1.0 CHEMICAL R and D

### 1.1 Leuco Dye Program

#### 1.1.1 D260

Small batches of D260 were purified during January to provide material for continued film studies. In addition, a 165 g sample of Michler's hydrol, purified by the benzene-petroleum ether technique, was converted to D259. The usual chromatographic purification of this material was carried out and after the D259 was eluted, the chromatographic column was treated with acetone followed by methanol to elute virtually all materials adsorbed on the column. The cuts taken in this way were concentrated to give fairly mobile fluids. These cuts will be examined by VPC on arrival of Horizons' new gas chromatograph.

Thin layer chromatographic (TLC) examination of the D260 delivered to us most recently by ChemSampCo revealed a gross impurity eluting just ahead of the D260. The impurity was definitely established as deleterious photographically, as reported in December. Elemental analysis of this impurity was correlated with infrared spectral data and physical properties. It is N,N,N',N'-tetramethyl benzidine (TMB). This compound arises by oxidative coupling of dimethylaniline in the preparation of Michler's hydrol and is carried through unreacted in the synthesis of D260. Work in January showed that the best way to remove this impurity (present in large quantity in ChemSampCo material) is by several triturations in hot ethanol in which D260 is only sparingly soluble. It was discovered that practically all of the TMB can be removed in this way by one alcohol trituration of material prepared in our laboratories, provided the Michler's hydrol had gone through at least one cyclohexane recrystallization prior to use in D260 synthesis.

##### 1.1.1.1 TMB Film Evaluation

The maximum amount of TMB that can be added to the 5/D7 system without changing its photoresponse is 1  $\mu$ g (10 ppm). Increasing the amount to 10  $\mu$ g (100 ppm) gives a film with lower maximum density (1.78 and a higher fog density (.24) than the normal control ( $\Delta D_{\max}$  -0.24,  $\Delta \text{Fog}$  +0.09). Addition

of 100  $\mu$ g (1000 ppm) of the impurity destroys the film completely (only a slight image can be seen with absolutely no fog after 300 seconds development).

Prior to the identification of TMB it was thought that this impurity was connected with speed decay since the photoresponses just described are similar in appearance to those of aging films. Attempts failed to detect its presence in decayed film by TLC. Now that its structure has been determined as TMB, it is realized that it cannot result from degradation of D260. Its presence to varying degrees in various D260 samples does, however, explain the varying uniformity of these samples with respect to photographic properties, while the extreme difficulty in separating it from D260 explains the difficulties which have been continually encountered in preparing photograde D260. There is still the possibility that other detrimental impurities are present and so work continues in addressing this problem.

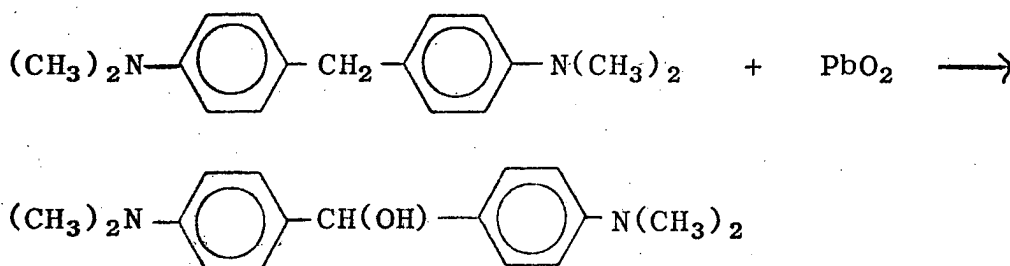
ChemSampCo has been kept informed of all chemical developments and is now following closely all their work by TLC. In addition, a benzene-petroleum ether recrystallization of Michler's hydrol was optimized during January and the details of the purification were transmitted to ChemSampCo. A double recrystallization from the medium serves to remove TMB completely (by TLC) as opposed to a double recrystallization from cyclohexane which leaves a small amount of TMB in the hydrol. Finally, ChemSampCo's most recent run has been followed closely by the project, by frequent phone conversations, and it appears to be coinciding very closely to our synthesis in the criteria of appearances, yields and TLC data.

#### 1.1.1.2 Michler's Hydrol Purification

The troublesome impurity in D260 was identified this month as N,N,N',N'-tetramethyl benzidine (TMB). Successful synthesis of clean D260 will be attained most easily by the use of Michler's hydrol free of TMB, rather than carrying the contaminant onto the D260 and attempting to separate it from this sensitive leuco compound, which is not easy and results in poor yields.

The commercial synthesis of Michler's hydrol is by the lead oxide oxidation of Michler's hydride:





The literature (Ref. 2) shows that TMB arises from the oxidation of dimethylaniline and of many other compounds containing a p-dimethylaniline moiety, such as Michler's hydrol and Michler's ketone. This leads to the postulate that Michler's hydrol prepared by an oxidation procedure would likely be contaminated with considerable quantities of TMB, easily confirmable by an examination of the crude Michler's hydrol purchased from Hilton-Davis.

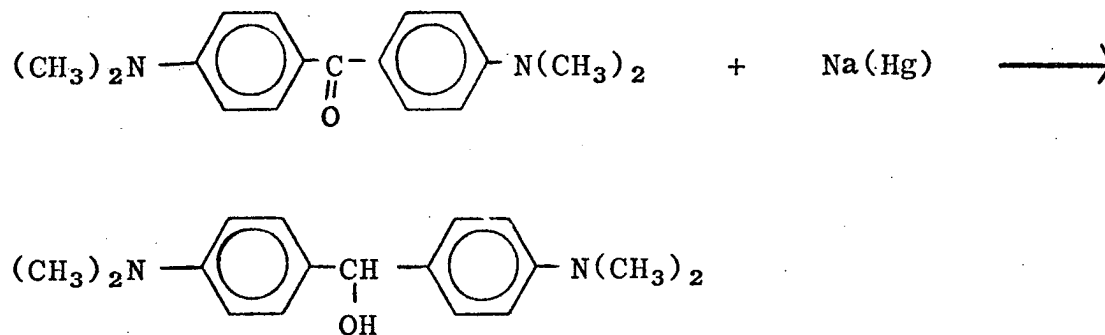
Purification of this crude Michler's hydrol from benzene by precipitation with petroleum ether has been demonstrated to give product free of TMB (by TLC). The hydrol can be oven-dried or dried by azeotropic distillation from benzene. Either way it can be purified by two precipitations in 65% overall yield.

Studies with "pure" D260 and pure TMB have demonstrated that TLC is capable of detecting as little as 50 ppm TMB in D260. This level falls between the film evaluated levels of 10 ppm (1  $\mu\text{g}$  - no noticeable effect) and 100 ppm (10  $\mu\text{g}$  - significant detrimental effect). Since all D260 to date has been made from purchased Michler's hydrol it is reasonable to expect that even "pure" D260 contains some amount of undetectable (less than 50 ppm) TMB. Thus even "pure" (photograde) D260 may be less than optimum. To test this possibility D260 must be synthesized in such a manner that no presence of TMB is possible. Two approaches are envisioned: one, the synthesis of Michler's hydrol by reductive rather than oxidative conditions; and two, the synthesis of D260 by an entirely different route which circumvents the use of Michler's hydrol. This approach should yield D260 containing at least some impurities different from those produced by the current synthesis. Comparative evaluations of D260 from two different routes will thus provide evidence concerning the relative importance of impurities other than TMB.

#### 1.1.1.3 Michler's Hydrol Synthesis

A clean synthesis of Michler's hydrol would be an acceptable alternative to the purification described above.

We have found that Michler's ketone can be reduced by sodium amalgam to the hydrol in 80% yield. The crude reaction product is white and dry and contains no TMB by TLC.



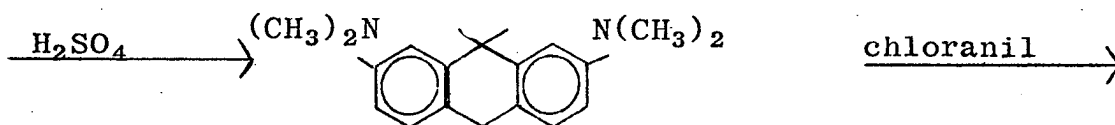
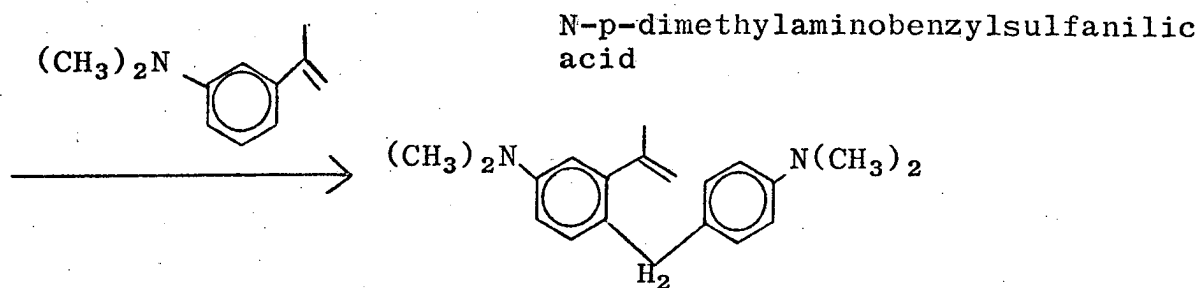
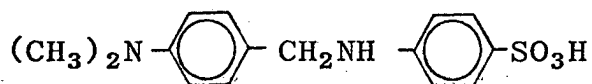
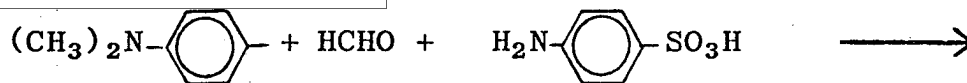
Reduction of Michler's ketone with  $\text{NaBH}_4/\text{AlCl}_3$  was unsatisfactory. A 3.5% yield was obtained but it was contaminated with Lewis acid which caused the product and filtrates to turn blue, even when handled in the dark at cold temperatures.

The synthesis by lead oxide oxidation of Michler's hydride (the commercial route) in progress last month led, as expected, to considerable contamination by TMB.

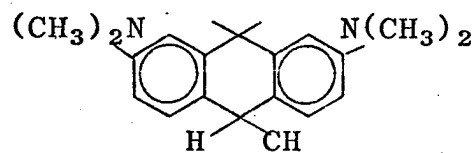
Attempted reduction of Michler's ketone with zinc and potassium hydroxide was ineffective, but the recovered ketone was extremely pure.

#### 1.1.1.4 Alternate Synthesis Route to D260

In another approach to the problem of dependable source of D260 of adequate purity, an alternate route was undertaken. This will be called the "Anthrone Route to D260." The entire sequence has been described by C. Aaron and C. C. Barker (Ref. 3).

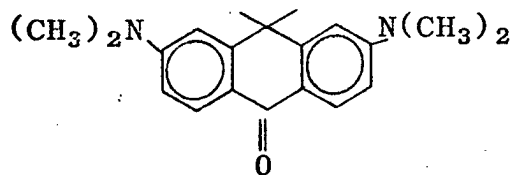


D263

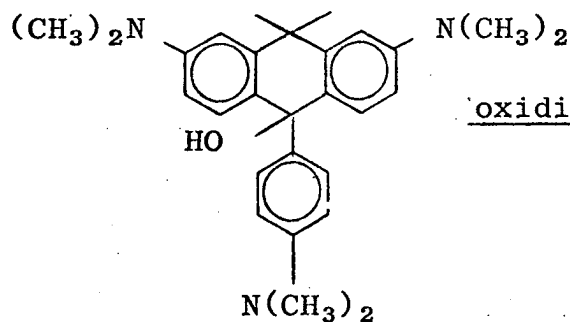
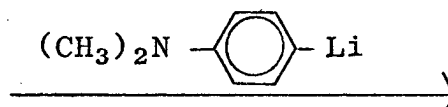


$\xrightarrow{\text{KO-t-Bu, benzophenone}}$

anthranol



anthrone



oxidize

D280

reduce

D260

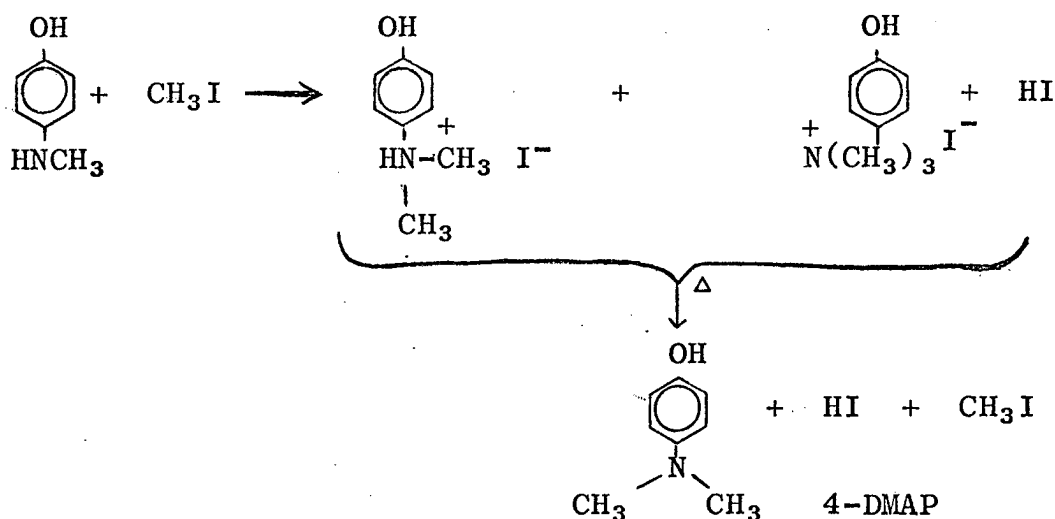
During January this route was carried to D263. About 100 grams of this intermediate were being purified at the end of the month.

Although multi-step, this route should be comparable to our present route. If the D260 formed is free of TMB, this route could be superior.

Synthesis of the anthrone would also give an intermediate which, using other metalaryls, would make available many other leuco anthracenes analogous to D260.

#### 1.1.1.5 D260 Decay Properties

The proposal for 325B (Ref. 1, p. 48) discusses the possible role of 4-dimethylaminophenol (4-DMAP) in speed decay. It should be remembered that 4-DMAP is a possible degradation product of D260 hydroperoxide and has been detected by mass spectrographic analysis in several samples of D260. 4-DMAP is not available commercially and was therefore prepared according to the following scheme.



For comparison, the three-isomer (3-DMAP) was purchased and purified. These materials are currently being evaluated.

#### 1.1.2 Other Leuco Dyes

Some preliminary film studies were begun with various samples of leuco crystal violet (LCV), leuco malachite green

(LMG), several LMG analogues, and D179, the leuco xanthene analogue of D260.

The results of these studies are too inconclusive to warrant discussion at this time. Further studies are planned for February and if the work is completed, the results will be discussed next month.

## 1.2 CB<sub>4</sub>

No CBr<sub>4</sub> purifications were carried out in January, but a 5 kg sample of CBr<sub>4</sub> was received from BDH. This material will not be opened to ordinary laboratory air, but will be handled exclusively under controlled environmental conditions.

A high vacuum line was put into operation for the sublimation and vacuum storage of CBr<sub>4</sub>. It was discovered that a number of modifications of this line were necessary and these were completed in January.

A sample of hexabromoethane was purified in January and turned over to film evaluation.

The purification and deterioration studies with Freeman and BDH CBr<sub>4</sub>'s are expected to commence in early February.

### 1.2.1 Film Additions of Halogen and Halogen Derivatives

#### 1.2.1.1 Hexabromoethane

Attempts to replace CBr<sub>4</sub> by hexabromoethane (523 mg and 311 mg) gave films which had no developable sensitivity (no image or fog produced after 15 minutes development time). Printouts of film containing 311 mg give a blue dye (maximum density 0.98, fog density 0.07). This suggests that the mechanism with C<sub>2</sub>Br<sub>6</sub> for printout image formation is different than CBr<sub>4</sub>, since apparently little or no D7 dye is produced to afford the usual deep magenta image. The result may be due only to the lower amounts of C<sub>2</sub>Br<sub>6</sub> used, however, and this possibility will be explored further by comparing with lower concentrations of CBr<sub>4</sub>.

Addition of 10 mg and 100 mg to the standard 5/D7 benzene system gave films with lower maximum densities and longer development times than standard.

#### 1.2.1.2 Hydrogen Chloride

Addition of trace amounts of hydrochloric acid to the standard control gave a film which was completely blotched (red background) with no image after 240 seconds development time.

#### 1.2.1.3 $\text{BF}_3 \cdot \text{OEt}_2$

Addition of trace amounts of boron trifluoride (a strong Lewis acid) to the standard control gave a film which was completely blotched (red background) with no image after 180 seconds development time.

#### 1.2.1.4 Bromine

Addition of trace amounts of bromine (10  $\mu\text{g}$ ) gave a film identical to the standard control. The 10 micrograms represents 8 ppm by weight of  $\text{CBr}_4$ . If  $\text{CBr}_4$  decomposes by disproportionation to give bromine and tetrabromoethylene ( $\text{C}_2\text{Br}_4$ ), the 10  $\mu\text{g}$  represents about 17 ppm decomposition on a molar basis. Thus, if the appearance of speed decay is due to the formation of bromine, then  $\text{CBr}_4$  must be decomposing to an extent greater than 17 ppm in less than an hour. Additional experiments are planned to determine the maximum amount of bromine which can be tolerated and to determine the effect of tetrabromoethylene.

The behavior of hydrochloric acid and boron trifluoride etherate indicate that rapid and extensive blotching may indeed be due to the presence of acid, by formation within the film (e.g. the decomposition of  $\text{CBr}_4$  to give hydrogen bromide -  $\text{HBr}$ ), or introduced either with the ingredients or by atmospheric contamination.

Positive proof that acid contamination from the atmosphere can cause rapid and total fogging (total blotch) occurred several months ago. A darkroom was accidentally contaminated with acetic acid vapors. A film run immediately prior to contamination was normal with an AEI well above 1.0. Subsequent

to the contamination the film fogged totally and immediately on attempted development, no image was discernible.

#### 1.2.1.5 CBr<sub>4</sub>- DABCO Complex and DABCO

DABCO is 1,4-diazabicyclo[2.2.2]octane. It has found great utility as a fog retardant in Horizons' duplicating film when used in very small quantities. It is a comparatively strong organic amine and apparently retards acid-caused fog by scavenging trace acids. Last year DABCO was found to provide acceptable photograde CBr<sub>4</sub> when present during the recrystallization, and during the period when the normal procedure failed to afford acceptable CBr<sub>4</sub>. Its use was soon abandoned, however, since no two batches of CBr<sub>4</sub> were identical.

DABCO forms a yellow crystalline, 1:1 complex with CBr<sub>4</sub>. An attempt to replace CBr<sub>4</sub> in the standard 5/D7 (benzene) system with an equivalent amount of this complex failed because of its insolubility.

Addition of less complex (85 mg which equals one-tenth as much) produced a slight blue image with a heavy blue fog after 360 seconds development. A printout gave the same blue image and blue fog. Decreasing the amount to 5 mg gave a maximum density (1.81) lower than the control and with a development time increased to 350 seconds. Printout gave a black image with blue fog. The maximum amount of complex that can be added to the 5/D7 system without changing its photosensitivity is 1 mg. Speed decay was not affected at this level.

Addition of 5 mg of DABCO to the 5/D7 system produced a blue image whose maximum density (.88) was much lower than normal with a much higher development time (600 sec.). Decreasing the amount to 100 µg also produced a film with lower maximum density (1.71) with slightly greater development times. Speed decay was not affected.

The formation of blue image in contrast to the usual deep magenta is easily explained in this case. DABCO, at least in larger concentrations, is scavenging acid, thereby preventing the formation of the red D7-dye. That DABCO is preventing the formation of D7-dye by some means other than a simple acid-base reaction cannot be excluded. It could be circumventing the normal mechanism(s) for image formation involving D7 by some means other than scavenging acid.

### 1.3 N-Oxide Program

During January six amine oxides (N2, N3, and N32-35) were either purified or prepared and purified for screening.

Thirty-one compounds of the N-oxide class (aromatic and aliphatic N-oxides, heterocyclic N-oxides, azo and azoxy compounds) have been tested photographically. Because of the large number of films to be evaluated, a special report of this study is currently being prepared and will be included in a future summary report.

### 1.4 Binder Studies

#### 1.4.1 Pressure Chemical Standard Polystyrenes

Three polystyrenes (mol. wt. - 110K, 200K, 390K from Pressure Chemicals, Pittsburgh, Pa.) were investigated as replacements for MX4500. The molecular weight 200K was found to resemble MX4500 most closely with respect to handling, development time and photosensitivity ( $\gamma$  and AEI speeds were the same). The higher molecular weight (390K) gave too thick a coating and developed too quickly while the lower molecular weight (110K) polystyrene gave too thin a coating and developed more slowly with less maximum density than control.

The 200K material will therefore be used for comparison to MX4500 in evaluating the effects impurities and end groups are having on photoproperties, particularly speed decay.

#### 1.4.2 Commercial Grade Impurity Studies

Past experiments with various commercial grade polystyrenes showed in several instances significant differences in photoproperties in comparison to MX4500. Borden's 230,000 gave slightly poorer films and Lustrex showed significantly poorer films. These two, along with MX4500 were sent to Waters Associates for separation of the low molecular weight (containing additives, impurities) fractions. These fractions, as benzene solutions, have now been received. The effect of these fractions will be evaluated using the Pressure Chemical 200K material.



In future work, it is also planned to investigate more closely the differences manifested by other molecular weight polystyrenes, particularly any differences in speed decay.

### 1.5 Environmental Studies

The control studies as outlined in the 325B proposal (Ref. 1, 3.3.6, p. 62) are not scheduled to begin until March.

#### 1.5.1 Air Sampling

The air sampling program (cf. ibid) for the identification of suspected air contaminants was begun in late December, 1971, and continues to date.

Some results are now available and are shown in Table 1. Results have been reported for oxidants, oxides of nitrogen, hydrogen halides, and arsenic. Of these, there is a positive correlation only for oxidants. The values quoted in the table are calculated for ozone, but the actual chemical form of the oxidant is not known. It could also be a radical or a volatile organic peroxide or hydroperoxide.

On the basis of the results so far reported, further testing for oxides of nitrogen and for arsenic has been discontinued.

Data on halogen acids, hydrogen selenide, and hydrogen telluride are still being awaited.

Although the results to date are incomplete and more data is certainly desirable, the correlation between "bad" films and oxidants is quite good, with only samples 18, 23 and possibility 26 being out of agreement. It is interesting that the worst films (nearly always totally fogged with little or no image formation) are obtained in a darkroom quite apart from the main film research area. This darkroom is adjacent to a lab where electrophotographic research is being conducted and where the equipment is known to produce ozone. The possibility that ozone is itself the major culprit is thus being investigated and it is hoped that February will see considerable clarification of the air contamination problem.

TABLE 1

## AIR SAMPLING RESULTS TO DATE

Includes results reported to us by National Loss Control through January 31, 1972. Samples corresponding to bad films are indicated by asterisk.

Sample Number	NO <sub>2</sub> , ppm	Oxidants mg/M <sup>3</sup>	X <sub>2</sub> , mg/M <sup>3</sup>	Arsenic, mg/M <sup>3</sup>
1	0.011		0.027	0.0004
2	15			< 007
3	19		04	04
4	10		07	< 007
5	16		08	< 007
6	07		29	02
7	05		21	11
8	11			< 007
9	17		19	< 007
10	15		03	
11	19			05
12	25	0.026	25	
13	06			
14	17	23	12	< 007
15	05	03	13	
16	14	26	44	< 007
17	10	23	13	< 007
18	07	46	15	04
19	12	17	14	< 007
20	07	10	18	< 007
21	07	13	22	< 007
22	12			
*23	10	21	20	< 007
24	12	49	08	< 007
25				< 007
*26	18	31	09	< 007
*27	12	65	11	< 007
*28	12	74	14	< 007

(continued)

TABLE 1 (continued)

Sample Number	NO <sub>2</sub> , ppm	Oxidants, mg/M <sup>3</sup>	X <sub>2</sub> , mg/M <sup>3</sup>	Arsenic, mg/M <sup>3</sup>
*29	0.008	0.095	0.012	< 0.00007
*30		52	10	04
*31	12	77	11	< 007
*32		74		01
*33				
*34				
*35		84	14	< 007
*36	08	58	19	< 007

## 1.6 Other Film Systems

No work has yet begun nor has any been scheduled until March. However, it would be desirable to compare the results being obtained with the 5/D7 system with the 5/DPA system. The 5/DPA system has been discussed on numerous occasions in the past (cf. Ref. 1, 3.3.3, p. 57). It will be remembered that the mechanisms of image formation with DPA, which is not a dye base, must be different than that with D7.

Interpretation of experimental results from 5/D7, such as have already been discussed in this report, would be considerably more meaningful if results could be compared to those from the 5/DPA system.

At present only one darkroom, the one which is environmentally controlled (cf. Ref. 1, 3.3.6, p. 62), is reliable and it is being used to capacity with studies on 5/D7. The adjacent darkroom provides much poorer and very inconsistent film results. It has been shown by numerous control and cross-over experiments with the adjacent, controlled room, that this is due to some form of atmospheric contamination. An attempt is being made to correct this situation. When it is corrected, plans are to begin immediately the standardization of the 5/DPA system.

## 1.7 Film Analysis of Decay Products

Due to the current manpower shortage in the chemistry group, little work has been done in this area. Some attempt was made to detect the presence of TMB in decayed film, but to no avail (cf. Section 1.1.1.1).

## 1.8 Dye Identification

Work is not scheduled to begin until May.

## 1.9 System Nonuniformities

### 1.9.1 Silicone Oil Addition (1807-30, 31, 35)

Eleven silicone oils were added to the 5/D7 system at various concentrations for evaluating the elimination of

"orange peel" (cf. Ref. 1, 3.3.10, p. 69). All but one, R631 (Union Carbide), behaved as DC510 (Dow Corning) and offered no advantages as a substitute. R631 silicone oil, however, eliminates "orange peel" and gives no significant difference photographically from the standard control. DC510, in contrast, gives higher  $\gamma$ 's, lower  $D_{max}$ 's and longer development times.

## 2.0 ENGINEERING

### 2.1 Calibration and Maintenance

All equipment used by 325B personnel continues to be calibrated and maintained on a regular basis so as to detect and correct any changes. There have been no major breakdowns or changes in any of the operational lab equipment during this reporting period.

### 2.2 Mechanical

The HID-2 red light development units are in final stage of either test or assembly. Three units have been completed and are undergoing tests; three more remain. The HID-2 has proven to be an effective laboratory red light development unit. The operational controls are simplified and the unit is greatly reduced in size. Preliminary testing of the three units indicate there is remarkable repeatability between units. It now appears that the development parameters of all six units will be identical.

### 2.3 Shelf Life

The first shelf life program to be undertaken is reactivation. Preliminary investigations of equipment, chemicals and mechanisms is underway. It is expected that reactivation studies will start as soon as a laboratory is available (see "Problems").

### Problems

The darkroom presently being used by engineering to conduct sensitometric and equipment evaluations has suffered a catastrophic contamination problem. At present the darkroom is useless for mixing, coating, exposing or developing 325B films. A test matrix has been completed whereby all steps of the process have been conducted in the engineering darkroom and the special environmental darkroom used by the chemistry group. It now appears that any of these steps

conducted in the engineering darkroom leads to a complete or partial failure of the system.

The chemistry group, being interested in defining the contaminant, has made a series of tests to determine if any correlation can be made between bad films and certain airborne contaminants. There have been no definitive results at this time. The darkroom has been sealed, has its own air conditioning unit and has been continuously cleaned by a Barnebey Cheney charcoal filtration device. There has been no improvement at this time. Although a number of theories have been put forth, none have proved to have good correlation with the film results. Engineering is attempting to circumvent this problem by construction of small isolated test chambers to be operated in various parts of the building to determine if without knowing the cause of the contamination laboratory work can continue. No shelf life studies in the form of reactivation or overcoating can be started until the contamination has been overcome; therefore, any engineering shelf life work must wait until a suitable chamber can be built and tested. It is anticipated this chamber will take no more than two weeks to build and occupy. Testing will probably take an additional week; hopefully reactivation work can be started before 1 March 1972.

### 3.0 PERKIN ELMER INTERFACE - QC/QA

#### 3.1 Supply of Film and Equipment

##### 3.1.1 Delivery of 325B Film

The first shipment of unexposed, sensitized, hand coated film cut to sample size was successfully delivered to P. E. on the 17th of January. The film speed and other aspects of film performance were essentially undiminished in the shipment. The hand coatings were made at [ ] on Friday, 14 January and checked out at an approximately 0.5 AEI. The only AEI check on 18 January at the P. E. facility was roughly 0.1 AEI. The deviations from the control samples run at [ ] if anything, indicate improved performance at the P. E. facility. Using the same processor at both facilities, the development times were 20 to 25% longer at P. E. with comparable fog and blotch. D<sub>max</sub> apparently was also better.

25X1

25X1

The shipment consisted of 60 1/2" wide strips of film with sufficient coating for exposure on a 21 step tablet. The samples were cut from 15 typical hand coatings, which used approximately one gram of the key compound, D260. The standard 325 formula 5/D7, was used and in every other respect the coatings are standard coatings, i.e., unsubbed on 5 mil Mylar, unfiltered, no silicone oil, and the typical film coating thickness in the .3 and .5 mil range. Because the shipment was to be used for setting up the P. E. lab, the best photo-grade quality of material was not used. At a later date the materials that would routinely give AEI's of 2.0 will be shipped. When necessary, especially for image evaluation, the cosmetic defects of undissolved D7 and streaking will be eliminated. The only other obvious defect in the first shipment, blocking of the image when used in the high speed mode, could not be corrected. Plans are being formulated for P. E. to investigate this effect.

In preparation for the second shipment, an effort was made to use ultrasonics to dissolve the D7 in the stock solution. The testing with appropriate size samples of D7 and polystyrene/benzene solution on a jewelry-equipment ultrasonic cleaner and on an industrial sized unit that delivers 600 watts, yielded no practical improvement. A marked improvement was made with a mechanical stirrer used at high speed for a longer time.



[REDACTED]

The second shipment was prepared on 31 January and was sent by airborne freight. Cosmetically this shipment will look better than the first. Sufficient controls were not run to identify the AEI speed. Indications are that it will be as fast or faster than the first shipment. In the printout mode the blue-density AEI speed is approximately  $1 \times 10^{-4}$ , which is typical of our best materials. Since the P. E. testing program to begin with is concerned primarily with printout tests, attempts to produce higher speeds were not carried out. The shipment consists of ten (10) sheets, 7 x 7-1/2" with approximately 30% of the area coated. Success of the transfer of this film has not been determined, as P. E. had not evaluated the films by the time of the preparation of this report. A delay had been experienced in shipment as the air freight company shipped to the wrong airport.

### 3.1.2 Delivery of Solvent Rinse

One gallon of solvent rinse was mixed at [REDACTED] and delivered with the first shipment.

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### 3.1.3 Delivery of Red Light Development Units

The older 4B unit with the 650 watt Sungun was delivered the 17th of January, in lieu of one of the HID-2 units, which will be completed in the beginning of February. The 4B unit was used for checking the first film shipment at [REDACTED], delivered to P. E. with the film, and used for checking the film there. Three people were instructed and trained in the use of this processor.

25X1

Along with the equipment and film, instructions included updating them in the latest technology with particular emphasis on the technology of interpretation of results since the film is in the experimental stage and not a final pilot coated product. Evaluation of the many subtle effects are as important as the straight forward readout of the sensitometry.

## 3.2 Cross Calibrations

Since the first shipment of film included a processing unit, the same processing unit could be used for quality control of

[REDACTED]

the materials before and after the coating run, as well as at the P. E. facility after delivery. In practice, QC of the development of the film is as important as QC of the grade of materials for the high speed mode. The HID-2 unit to be delivered will be one of a series of six which will have been made as identical as the state-of-the-art will allow. The six units will be thoroughly checked out and cross calibrated before the one is shipped. The same care will be taken for shipment of lamps for replacement.

The first significant discrepancy in photographic response between [REDACTED] and P. E. to be identified, was in densitometry. This was first identified when the two samples brought with the first shipment were read on the P. E. densitometer, which is a TD-102, the same model as used in the 325B project area at [REDACTED]. Reading the standard calibration tablets supplied with each TD-102 does not reveal any discrepancy between the two densitometers. The cross calibration using a 325 step tablet processed at [REDACTED] and one processed at P. E. shows that the [REDACTED] densitometer is reading consistently lower than the unit at P. E. The use of an Ektacolor color tablet also indicates that the P. E. densitometer is reading higher, but this tablet does not show as great a discrepancy. That the reading of density of 325B films is so dependent on the color filter of the densitometer has been proven before in studies with a radiometer, with a series of light-table colors, and with a series of source colors for dapping onto PH Type 2000 film. Because of this, a special standard with sharp color cut-ons and relatively narrow wavebands may have to be setup for calibrating densitometers for 325B film.  $D_{max}$ 's at P. E. are being read at the 3.5 range, while the  $D_{max}$ 's at Horizons are typically 2.5 and on rare occasions, 2.7. As of now the two noteworthy factors are: one, the real densities produced at their facility apparently are higher than here; and two, if their densitometer is found to be incorrect, the filter color that is used to read these high densities should become the established one, even though it isn't the standard MacBeth product.

### 3.3 Evaluation of Production, Shipping and Contamination

The use of hand coatings for the test film is tedious and expensive. The procedure worked out for the first shipment apparently was successful. Particular care was made in weighing, mixing and production of a film in the one room that has consistently low levels of airborne contamination.

Attention was also given to packing the film in dry ice as quickly as possible after coating. For the case of the first shipment, the time from coating to freezing was on the average 4 to 4-1/2 minutes. For the second shipment the time was reduced to 1 minute and 45 seconds on the average. As the shelf life studies proceed, it should be possible to relax this requirement. The film strips were placed in individual thin cardboard boxes. This type of box has fairly good heat transfer properties. About 15% of the samples were used for test purposes the first two days, all of which were satisfactory. In the two weeks that it took to use the rest of the supply, about 10% were found to be fogged. This may be an indication of the problem of CO<sub>2</sub> from the dry ice replacing the air during storage. Experiments will be carried out to definitely prove this. It may also indicate that one condition for providing required shelf life is to place the film in a special atmosphere such as a higher concentration of oxygen. The second shipment was not cut to sample size because the user can achieve greater efficiency by cutting the sheets to smaller sizes to fit their particular exposure requirements. Because of the problem of air contamination in some of the [ ] labs, the air at the P. E. facility was another concern. Based upon the first experiments, the air at P. E. is not contaminated with respect to our film. In fact, the better performance at P. E., if that is the case, may be due to the reduced contamination in the P. E. air system. When all the air sampling data at [ ] is in and reduced, the knowledge gained will be used to sample and check the contamination level at the P. E. facility.

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### 3.7 QC/QA

The supply of quantities of photograde materials has been fairly reliable over the last several months. Although the quantity of materials on the shelf has never been great, they have been consistent with the lead times now needed for production of more material. The quantity and quality of the D260 supplied by ChemSampCo has not been good, although the solutions to their problems seem near at hand.

The achievement of analytical techniques for quality control has shown considerable progress. The thin layer chromatography experience has reached a point at which the photograde quality of the material can be determined before testing in the coating lab. The "yellow spot" on the TLC (thin layer chromatography) samples which has been correlated

with poor performance, has now been identified. It is described in the chemistry section of this report. The TLC technique is now being used at ChemSampCo for control of their intermediates and products before shipment. We have had to accept less than quality grade material from ChemSampCo in order to keep our supply ahead of needs. The resulting loss to us was lower yield of final photograde product after passing through the purification column.

Air contamination has been identified as a separate problem from the synthesis and purification problem. A film produced in an "uncontaminated" room and stored for later use can eventually go "bad" if taken out of storage, exposed and processed in a "contaminated" lab. The progress in identification of the impurity in the air is reported in the chemistry section. The means for controlling the problem with the one room that has been consistently good is described in the engineering section. The room has been controlled to a constant humidity and temperature, the air flow from outside the room has been restricted, and the air within the room is filtered with a Barnebey Cheney activated charcoal filtration system.

## PROBLEMS

- 1) As of January 31, no official verbal approval to proceed on this program had been received. Several large laboratory items required for the shelf life investigations have not been ordered awaiting this approval.
- 2) Three new hires for this effort have not been secured pending the verbal go ahead. Further delay in securing manpower and equipment will seriously reduce project performance on the items listed in the detailed Work Statement contained in the proposal and effect performance vs. schedule times.
- 3) The engineering darkroom used for coating and reactivation studies reached a prohibitive contamination level. The air conditioning and filtration system was in continuous operation 24 hours per day. This has necessitated a major cleanup of the room and construction has started on a separate sealed room as backup for the main engineering darkroom.

## PLANS FOR NEXT REPORTING PERIOD

Continue to work according to the detailed Work Statement within the constraints as given in problems section.

## FINANCIAL

Require official verbal go ahead on this project.

REFERENCES

- 1) "[ ] Free Radical Camera Speed Film Proposal,  
Extension of Shelf Life and Reduction of System  
Nonuniformities," Proposal No. 1185, [ ]  
January 1, 1972 through December 31, 1972. 25X1
- 2) Rosenstiehl, Bull. Soc. Chim. France (3) 13, 273 (1895). 25X1
- 3) C. Aaron and C. C. Barker, J. Chem. Soc. 1963, 2655.

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